# Liquid immersion deep-ultraviolet interferometric lithography

J. A. Hoffnagle,[a] W. D. Hinsberg, M. Sanchez, and F. A. Houle
*IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099*

An apparatus for deep-ultraviolet interferometric lithography is described, in which the interfering beams illuminate the substrate through a fused silica prism and a layer of index-matching liquid. The liquid-immersion technique was found to be compatible with a commercially available, chemically amplified photoresist. The apparatus was used with a 257 nm light source to write gratings having a period of 97 nm and linewidth of approximately 40 nm. © 1999 American Vacuum Society. [S0734-211X(99)08006-3]

## I. INTRODUCTION

Interferometric lithography has been shown to be a powerful technique for the generation of large, periodic patterns such as gratings, grids, and arrays of holes or posts.[1-3] Because it provides well-defined illumination with high contrast over a large range of spatial frequencies, interferometric lithography is also well suited to the study of the fundamental physical chemistry of the photolithographic development process.[4,5] Since one of its most attractive features is the capability to write a pattern with a single, very high spatial frequency, it is obviously of interest to consider all available means of extending the limits of interferometric lithography to generate the smallest possible features.

In the simplest implementation of interferometric lithography,[6] two mutually coherent plane waves of wavelength $\lambda$ are incident on a substrate in such a way that their wavevectors are coplanar and each make an angle $\theta$ with respect to the normal to the substrate, as shown in Fig. 1. Interference of the two plane waves produces a sinusoidal intensity distribution, or grating pattern, with periodicity $\Lambda$ given by

$$\Lambda = \lambda/2 \sin(\theta). \tag{1}$$

As $\theta$ approaches 90°, $\Lambda$ approaches the limiting value of $\lambda/2$, which corresponds to the highest spatial frequency that is theoretically achievable with freely propagating light beams of a given wavelength. To write finer gratings, one can take advantage of the reduction in wavelength of light propagating through an optically dense medium, in which case

$$\Lambda = \lambda_0/2n \sin(\theta). \tag{2}$$

where $n$ denotes the index of refraction of the medium in which the interference takes place and $\lambda_0$ is the vacuum wavelength of the interfering beams. The liquid immersion technique widely used in optical microscopy immediately suggests itself as a method to realize interference in an optically dense medium. We have constructed an exposure system that implements liquid immersion interferometric lithography with deep ultraviolet (UV) light (257 nm) and a

---

[a]Electronic mail: hoffnagl@almaden.ibm.com

commercially available chemically amplified photoresist. The results show that the predicted improvement in grating pitch can be achieved with a simple interferometer.

## II. APPARATUS

The most straightforward means of generating two-beam interference in an optically dense medium while at the same time allowing large values of $\theta$, is to couple the beams through the equal faces of an isosceles prism,[7-9] as shown in Fig. 2. Note that although the figure is drawn so that the beams enter the prism normal to the input faces, oblique incidence is also possible. In order to couple the light efficiently into the photoresist, the space between the prism and the substrate was filled with index-matching liquid. (In principle, evanescent wave coupling is also possible, but this uses the optical power less efficiently and requires an extremely flat substrate and precise positioning of the prism relative to the substrate, whereas liquid immersion is both efficient and simple to realize.) The liquid must satisfy several requirements: it must have low absorption for the wavelength being used; its index of refraction must be a reasonably good match to that of the prism, as discussed below, and it must be chemically compatible with the photoresist. The goal of using a chemically amplified resist, in which small amounts of photogenerated acid catalyze the deprotection reaction, combined with the need for deep-UV transparency, led us to consider chemically neutral compounds such as straight-chain and cyclic alkanes.

To better understand the role of the matching liquid, we consider more closely the interface between the prism, liquid, and substrate, shown schematically in Fig. 3. Here, $n_1$ and $n_2$ denote the indices of the prism and the index matching liquid, and $\theta_1$ and $\theta_2$ are the corresponding propagation angles with respect to the substrate normal. As drawn, $n_2 > n_1$, but the same considerations apply for $n_2 < n_1$, provided that $\theta_1$ is less than the critical angle for total internal reflection. The liquid layer is assumed to be thick enough that one can neglect evanescent coupling and other thin-film effects, which is reasonable for the conditions of our experiment. The periodicity of the interference pattern at the substrate is given by applying Eq. (2) to the beams incident on the substrate.
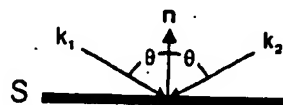
FIG. 1. Schematic drawing of two-beam interference.

$$\Lambda = \lambda_0/2n_2 \sin(\theta_2) \quad (3)$$

$$= \lambda_0/2n_1 \sin(\theta_1). \quad (4)$$

One sees that the grating period is *independent* of the refractive index of the plane-parallel liquid layer: the change in wavelength according to $\lambda = \lambda_0/n$ is exactly canceled by the change in $\theta$ due to refraction at the glass-liquid interface. In practice it is desirable for the glass and liquid indices to be approximately equal, in order to minimize reflections at the interface. We thus conclude that $n_2 = n_1$ is the most desirable index for the matching liquid. The amount of index mismatch that can be tolerated depends on the desired value of $\theta$ and the acceptable reflectivity of the glass-liquid interface. For instance, at $\theta = 60°$ an index mismatch of 3% results in less than 0.5% reflectivity for *s* polarization.

To demonstrate liquid immersion interferometric lithography, we adapted the apparatus described in Ref. 4. The light source is a continuous-wave (cw) $Ar^+$ laser operating on the 514.5 nm transition, incorporating an intracavity frequency doubling crystal of beta-barium borate. The resulting 257 nm beam is spatially filtered, collimated, and about 1% of the intensity is picked off with an uncoated fused silica substrate and directed to a photodiode for exposure control. A dielectric beamsplitter generates two beams of equal intensity (accuracy approximately 2%), which are redirected by mirrors to the coupling prism as shown in Fig. 2. The prism is fabricated from fused silica ($n = 1.50$ at 257 nm) with apex angle $\alpha = 90°$. The index-matching liquid was cyclo-octane. From a measurement of the displacement of a collimated beam by a tilted cuvette of cyclo-octane we estimate $n = 1.51$ for the index of refraction at 257 nm. The excellent match to fused silica results in negligible reflectivity. The
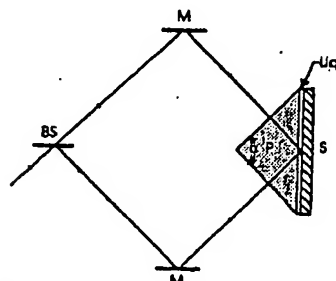


FIG. 2. Geometry of a coupling prism used to achieve two-beam interference in an optically dense medium. The components are a beamsplitter (BS), two folding mirrors (M), prism (P) with apex angle α, index-matching liquid (Liq), and substrate S.
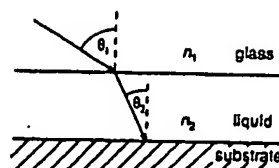
FIG. 3. Detail of the silica-liquid-substrate interface. For simplicity, only one of the interfering beams is shown, and the layers of photoresist and BARL are omitted, the interference pattern being assumed to exist at the surface of the substrate.

measured attenuation of the beam corresponded to an absorption coefficient (base *e*) of 2.44 $cm^{-1}$, and no noticable UV-induced fluorescence was observed. No attempt was made to purge the sample of oxygen for this measurement. The interferometer was adjusted so that $\theta = 61.3°$. Under these conditions Eq. (2) predicts $\Lambda = 97.5$ nm.

## III. EXPERIMENTAL RESULTS

The apparatus described above was used to expose films of Shipley UVII-HS, a commercial, chemically amplified resist designed for 248 nm exposure. The resist solution was thinned to 25% of its original solids content with propylene glycol methyl ether acetate. No modifications were made to the usual preparation and development process: the resist film was applied with a thickness of 140 nm over a 90-nm-thick antireflection layer (BARL 900) and baked for 60 s at 130°C. After exposure, the film was baked for 90 s at 140°C and developed in Shipley CD-26 developer for 20 s.

Chemically amplified resists are notorious for their extreme sensitivity to parts-per-billion traces of basic contaminants. We found that our supply of high-purity cyclo-octane (Fluka purum grade) apparently contains basic contaminants at a level sufficient to affect lithographic imaging, producing a skin at the resist interface that is characteristic of base contamination.[10] Treatment of the liquid with chromatography-grade silica gel followed by filtration eliminated this effect.

A scanning electron micrograph of a developed photoresist film is shown in Fig. 4. The period of the grating pattern is consistent with the expected value of 97 nm, and the lines of photoresist are approximately 40 nm wide. The root-mean-square (rms) variation in the line width is approximately 5 nm. To the best of our knowledge, these are the smallest features that have been written optically in a chemically amplified photoresist. Achromatic interferometric lithography has been used to write 100 nm period gratings in poly(methylmethacrylate) (PMMA);[1] this approach uses beams with $\lambda_0 = 193$ nm propagating in air and requires an extremely accurately constructed grating interferometer to produce clean interference patterns in view of the poor coherence properties of the ArF laser.

The fact that our exposures yielded a clear grating pattern in the developed photoresist has important implications for the role of acid diffusion in the resist. Current estimates of
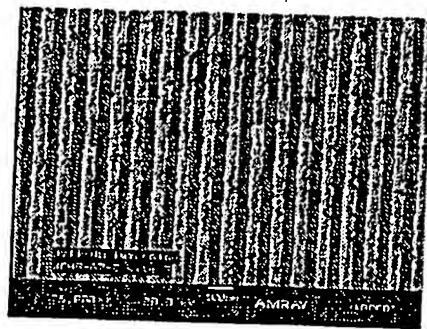
Fig. 4. Scanning electron micrograph of line-space array printed in Shipley UVII-HS chemically amplified photoresist by liquid immersion deep-UV interferometric lithography.



Fig. 5. Scanning electron micrograph of line-space arrays with identical geometry and total dose (2.1 mJ/cm²) but different laser polarization: (a) *s* polarization; (b) *p* polarization.

acid diffusion coefficients in deep-UV chemically amplified photoresists are in the range of $10^{-11}$–$10^{-13}$ cm²/s at 90 °C.[11] A value of $10^{-13}$ cm²/s, in the center of this range, would correspond to a lower limit on the diffusion length of 70 nm, if all image blurring were due to diffusion alone. This would predict a spreading of the nominal 50 nm spaces to 120 nm. If this magnitude of the diffusion coefficient were correct, we should not have seen any features at all. Clearly the apparent diffusion length is much smaller, with an upper limit of order 50 nm based on the well-resolved 50-nm-wide lines and spaces in Fig. 4. This extent of spreading would correspond to an upper limit to the diffusion coefficient of $4 \times 10^{-14}$ cm²/s at the significantly higher temperature of 140 °C. This is consistent with our independent measurements of diffusion in a closely related model system.[12]

Flagello and Milster[13] have observed that interferometric lithography can serve as a useful model of imaging photolithographic systems, and performed an interferometric experiment to demonstrate the importance of polarization effects for high-numerical-aperture exposure (NA = 0.85). In our experiment the NA is even higher, so one expects the polarization effects to be still more dramatic. To obtain the results shown in Fig. 4, the interfering beams were *s* polarized. For a direct test of the effect of beam polarization, $\lambda/2$ plates were inserted in the interfering beams, allowing the polarization to be varied without changing any other experimental conditions. Exposures were made with $\theta = 48.3°$ (NA = 1.12), resulting in $\Lambda = 115$ nm according to Eq. (2). The developed photoresist patterns shown in Fig. 5, indicate that while the exposures with *s*-polarized light give a clean grating pattern, the *p* polarized exposures have almost no relief. This is consistent with the expected contrast reduction for *p*-polarized light and our earlier experiments[4,5] showing that poor contrast leads to a large degree of line-edge roughness and thickness loss.

## IV. DISCUSSION AND CONCLUSIONS

We have shown that liquid immersion interferometric lithography can be performed with a commonly used, chemi-
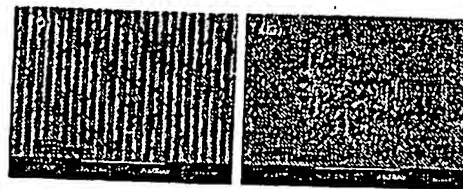
cally amplified photoresist, without any materials composition or process modifications. Using a 257 nm light source, gratings were written which would have required a vacuum wavelength of approximately 193 nm, had conventional interferometric lithography been used. By taking advantage of the wavelength reduction in an optically dense medium, we effectively use a wavelength of $\lambda_0/n$, or 171 nm, to write the interferometric grating. The developed patterns are much cleaner when *s* polarization is used, which is consistent with the expected contrast degradation for *p* polarization.

It is natural to ask whether these results can be extended to write even smaller features. One approach would be to further increase *n*. The only material of high optical quality which is in widespread use in the optical industry, is transparent at deep-UV wavelengths, and has a higher index of refraction than fused silica is sapphire, with $n = 1.83$ at 257 nm. The birefringence of sapphire presents some difficulties maintaining the polarization purity of the interfering beams, but one could cut the prism in such a way that both beams propagate as ordinary rays. A more fundamental limitation, however, is due to the refractive index of the photoresist, $n_r$. If the coupling prism has a higher index than the photoresist, rays incident on the resist film with large $\theta$ will be totally reflected. Of course, there would still be evanescent coupling to the photoresist, but this would be relatively weak and would vary strongly across the thickness of the resist layer. If one excludes the use of evanescent coupling, then the photoresist index sets a lower limit

$$\Lambda_{min} = \lambda_0/2n_r \qquad (5)$$

on the grating pitch that can be achieved, regardless of the indices of the coupling prism and matching liquid. For the Shipley UVII-HS resist that we used $n_r = 1.68$, which means that even if materials with higher indices were available, the reduction in grating pitch relative to the fused silica/cylcooctane system would only be about 12%.

There remains the possibility of extending the liquid immersion technique to lower $\lambda_0$. Though there is little data on the optical constants of liquids at around 200 nm, it seems likely that alkanes and saturated cyclic hydrocarbons could be found which would be sufficiently transparent and have the correct index of refraction to serve as a matching layer for fused silica. It is therefore probable that an extension of this technique to the ArF wavelength range would be feasible.

*Note added in proof.* After this paper was submitted, we succeeded in writing gratings with 89 nm period, by increasing $\theta$ to 73°.

[1]A. Yen, E. A. Anderson, R. A. Ghanbari, M. L. Schattenburg, and H. I. Smith, Appl. Opt. 31, 4540 (1992).

[2]T. A. Savas, S. N. Shah, M. L. Schattenburg, J. M. Carter, and H. I. Smith, J. Vac. Sci. Technol. B 13, 2732 (1995).

[3]X. Chen, S. H. Zaidi, S. R. J. Brueck, and D. J. Devine, J. Vac. Sci. Technol. B 14, 3339 (1996).

[4]W. Hinsberg, F. A. Houle, J. Hoffnagle, M. Sanchez, G. Wallraff, M. Morrison, and S. Frank, J. Vac. Sci. Technol. B 16, 3689 (1998).

[5]M. I. Sanchez, W. Hinsberg, F. A. Houle, J. Hoffnagle, H. Ito, and C. Nguyen, Proc. SPIE 3678, 160 (1999).

[6]M. C. Hutley, *Diffraction Gratings* (Academic, London, 1982).

[7]A. Labeyrie, Proc. Conf. Optics, Marseille Centre Nat. d'Etudes Spatiales, 1967 (cited in Ref. 6).

[8]C. V. Shank and R. V. Schmidt, Appl. Phys. Lett. 23, 154 (1973).

[9]W.-T. Tsang and S. Wang, Appl. Phys. Lett. 24, 196 (1974).

[10]S. D. MacDonald, W. D. Hinsberg, H. R. Wendt, N. J. Clecak, C. G. Willson, and C. D. Snyder, Chem. Mater. 5, 748 (1993).

[11]G. M. Wallraff and W. D. Hinsberg, Chem. Rev. (in press).

[12]G. M. Wallraff, W. D. Hinsberg, F. A. Houle, M. Morrison, C. Larson, M. Sanchez, and J. Hoffnagle, Proc. SPIE 3678, 138 (1999).

[13]D. G. Flagello and T. D. Milster, Appl. Opt. 36, 8944 (1997).